Synthesis and Characterization of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) Complexes with new Tridentate (ONO Donor) Schiff Base Ligand

Enaam MajeedRasheed

Al-Mustansiriyah University, College of Science, Department of Chemistry

ABSTRACT

In this work tridentate Schiff base was prepared from the reaction of 4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one with isatin. The product (L) was characterized by (FT-IR), (UV-Vis) spectroscopy and elemental analysis (C.H.N). (L) has been used as a ligand to prepare number of metal complexes with Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II). The prepared complexes were isolated, characterized and their structural geometries were suggested by using elemental analysis (C.H.N), flame atomic absorption technique, FT-IR and UV-Vis spectroscopy, in additional to magnetic susceptibility and conductivity measurements, metal to ligand [M:L] ratio was obtained for all complexes in ethanol using molar ratio method, which gave comparable results with those obtained for the solid complexes.

Keywords: Synthesis, characterization, pyrazolin derivative, isatin, Schiff base and transition metal complexes.

INTRODUCTION

A large number of Schiff bases and their complexes have been studied for their interesting and important class of ligands in coordination chemistry[1]. Schiff base derivatives are known to possess biological activites[2]. The development of the field of bioinorganic chemistry has been increased the interest in Schiff base complexes, since, it has been recognized that many of these complexes may serve as models for biologically important

species [3, 4]. Coordination compounds derived from isatin have been reported to possess antibacterial, antifungal, analgesic and anti-inflammatory activity [5-7]. Also, Schiff bases of pyrazoline derivative and its complexes have a variety of applications in biological, clinical, analytical and pharmacological areas [8]. The present paper describes synthesis and characterization of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes of Schiffbase derived from the condensation of 4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one with isatin.

Experimental

All chemicals were of highest purity and were used as received.

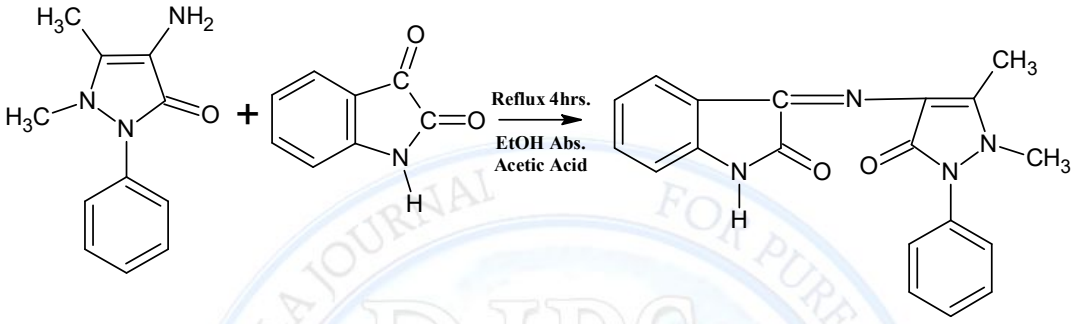
Physical Measurements and Analysis :

Melting points were recorded on Gallenkamp melting point apparatus and were uncorrected. FT-IR spectra were recorded using FT-IR 8300 Shimadzu in the range of (4000-200)cm^{-1}. Samples were measured as CsI disc. Electronic spectra were obtained using UV-1650pc. Shimadzu spectrophotometer at room temperature. The measurements were recorded using a concentration of 10^{-3}M of the complex in dimethylformamide as solvent. Micro analytical data for C.H.N were obtained using EA-034, mth. Flame atomic absorption was obtained using Shimadzu corporation model 6809. Conductivity measurments were obtained using corning conductivity meter 220. These measurements were obtained in DMF as solvent using concentration of 10^{-3}M at 25°C. Magnetic susceptibility measurements were obtained at 25°C on the solid state applying Faraday's method using Bruker BM_6 instrument.

Synthesis of Schiff Base Ligand (L) :

The synthesis of Schiff base is schematically presented at scheme 1. An ethanolic solution of 4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (2.03g, 0.01mole) was added to an ethanolic solution of Isatin (1.47g, 0.01mole) with few frops of glacial acetic acid. The mixture was refluxed for 4hrs., the solvent was removed and solid product was collected and

crystallized from ethanol. Some of the physical and chemical properties of the prepared ligand are listed at table 1.



(L)

Scheme 1

Synthesis of Schiff Base Complexes (E_1-E_6) :

Ethanolic solution (10ml) of each one of the following metal chloride (1mmole), $MnCl_2.4H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $ZnCl_2$ and $CdCl_2$ was added to an ethanolic solution (10ml) of (0.332g, 1mmole) of (L) with stirring. The mixture was heated under reflux for 2hrs. during this time a precipitate was formed. The product was isolated by filtration, washed several times with hot ethanol and then dried under vacuum. Some of the physical and chemical data of the prepared complexes are shown at table 1.

Study the Complexes Formation in Solution :

Complexes of (L) with metal ions were studied in the solution using ethanol as solvent in order to determine [M:L] ratio in the complex following molar ratio method [9]. A series of solution were prepared having a constant concentration 10^{-3}M of the metal ion and (L). The [M:L] ratio was determined from the relationship between the absorption of the absorbed light and the mole ratio of [M:L]. the results of complexes formation in solution were listed at table 1.

RESULTS AND DISCUSSION

A. Elemental Analysis :

The physical analytical data of (L) and its metal complexes are given at table 1, in a satisfactory agreement with the calculated values. The suggested molecular, which are formulas also supported are subsequent spectral and molar ratio, as well as, magnetic moment.

B. Infrared Spectroscopic Study :

The IRspectra provide valuable information regarding the nature of functional group attached to the metal atom. The prominent infrared spectral data of Schiff base and its metal complexes are presented at table 2. The IR spectra of the Schiff base exhibited characteristic band due to carbonyl group of pyrazolin ring $\upsilon_{C=O}$ and carbonyl group of Isatin ring $\upsilon_{C=O}$ at 1651 cm^{-1} and 1726cm^{-1} respectively. In addition to characterizing new band at 1585 cm^{-1} of azomethine group $\upsilon_{C=N}$ are utilized to confirm the structure of (L) [10], table 2. A comparison of the infrared spectra of the free ligand and all metals Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes exhibited the band of carbonyl group of pyrazolin ring in the region 1618-1630 cm^{-1} showing shift of band to lower wave numbers indicating that the carbonyl oxygen is coordinate to the metal ion [11]. The band of carbonyl group of Isatin ring in the region 1700-1714 cm^{-1} in the metal complexes show shift to the lower wave numbers confirms that the carbonyl oxygen is coordinate to the metal ion [12]. In addition to, all metal complexes exhibited the band of $\upsilon_{C=N}$ in the region 1558-1570 cm^{-1} showing band shift to the lower wave numbers indicate that theazomethine nitrogen is coordinate to all metal ion [13]. The metal Ni(II), Zn(II) and Cd(II) complexes show broad band in the region 3310 cm^{-1} to 3440 cm^{-1}, which may be assigned to υ_{O-H} of coordinated water. The new bands in the region of 434-459 cm^{-1} and 575-592 cm^{-1} in the spectra of the complexes are assigned to stretching frequencies of (M-O) and (M-N) bands respectively [13].

Table 2: Characteristic Stretching Vibrational Frequencies (cm^{-1}) located in the FT-IR of (L) and its Metal Complexes

Comp. No.	υOH of Water	$\upsilon_{C=O}$ of Isatin	$\upsilon_{C=O}$ of Pyrazolin	$\upsilon_{C=N}$Azomethine	M-N	M-O
(L)	-	1726	1651	1585	-	-
E_1	-	1705	1624	1560	575	437
E_2	-	1701	1620	1558	590	450
E_3	3310 br.	1700	1625	1565	578	434
E_4	-	1714	1620	1563	584	440
E_5	3380 br.	1710	1618	1570	588	445
E_6	3440 br.	1707	1630	1568	592	459

C. Electronic Spectra, Magnetic Moment and Conductance Studies :

The UV spectrum of Schiff base (L) showed intense bands at 226 nm, 265 nm, which belong to $\pi \rightarrow \pi^*$, 304 nm, 345 nm, which belong to $n \rightarrow \pi^*$ [10, 14]. The electronic spectrum gives information on the electronic environment of the metal. The splitting of d orbital and in turn the structure expected for the the complexes. Table 3 gives information on the various electronic obtained for the complexes.

E_1: Electronic spectra of the Mn(II) complex display absorption bands at 17819, 26052 cm^{-1} characteristic of octahedral geometry corresponding to $^6A_1g \rightarrow {}^4T_2g$ (G), $^6A_1g \rightarrow {}^4E_1g$, ^4A_1g (G) transitions, respectively [15]. The complex shows magnetic moment in the range 5.61 B.M. referes to high spin complex.

E_2: The absorption spectra of Co(II) complex show three transitional bands in the region 12512, 16713 and 23054 cm^{-1}. These transitions may be assigned to $^4T_1g \rightarrow {}^4T_2g$ (F), $^4T_1g \rightarrow {}^4A_2g$ (F) and $^4T_1g \rightarrow {}^4T_1g$ (P) respectively. The transitions correspond to the octahedral geometry of the complex [16]. The magnetic moment of the solid complex 4.77 B.M. indicating a high spin octahedral geometry.

E_3: The electronic spectra of Ni(II) complex exhibited three bands at 16528, 22421 and 27593 cm^{-1}, which are attributed to $^1A_1g \rightarrow {}^1A_2g$, $^1A_1g \rightarrow {}^1B_1g$ and $^1A_1g \rightarrow {}^1Eg$ transitions, respectively. The magnetic moment of the solid complex is diamagnetic indicating a square planer geometry [17].

E4: The electronic spectra of Cu(II) complex showed on band at 15985 cm^{-1} attributable to $^2Eg \rightarrow {}^2T_2g$ transition in the octahedral geometry [18]. The magnetic moment value was 1.79 B.M. corresponds with one unpaired electrons, table 3.

E_5, E_6: The UV-Vis spectra of Zn(II) and Cd(II) complexes show no absorption peak at range 380-1000 nm that indicates no d-d electronic transition happened d^{10} system in visible region, which is a good result of Zn(II) and Cd(II) tetrahedral complexes [19, 20].

The higher value of molar conductivity (Λ_m) in DMF indicates the electrolytic nature behavior of these metal complexes.

Table 3: Electronic Spectra, Conductance (in DMF) and Magnetic Moment (B.M) for (L) and Its Metal Complexes

Comp. No.	Bands cm^{-1}	Assignment	Molar Cond. $Ohm^{-1}.cm^2.mol^{-1}$	μeff B.M.	Suggested Structure
(L)	44247 37735 32894 28985	$\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ $n \rightarrow \pi^*$	-	-	-
E_1	17819 26052	$^6A_1g \rightarrow {}^4T_2g$ (G) $^6A_1g \rightarrow {}^4Eg, {}^4A_1g$ (G)	157	5.61	Octahedral
E_2	12512 16713 23054	$^4T_1g \rightarrow {}^4T_2g$ (F) $^4T_1g \rightarrow {}^4A_2g$ (F) $^4T_1g \rightarrow {}^4T_1g$ (P)	166	4.77	Octahedral
E_3	16528 22421 27593	$^1A_1g \rightarrow {}^1A_2g$ $^1A_1g \rightarrow {}^1B_1g$ $^1A_1g \rightarrow {}_1Eg$	128	Zero	Square Planer
E_4	15985	$^2Eg \rightarrow {}^2T_2g$	130.9	1.79	Octahedral
E_5	24876 33898	L → M (C.T)	135	Zero	Tetrahedral
E_6	23988 37593	L → M (C.T)	119.5	Zero	Tetrahedral

Fig. (1) : FT-IR. Spectrum of (L) ligand ($C_{19}H_{16}N_4O_2$)

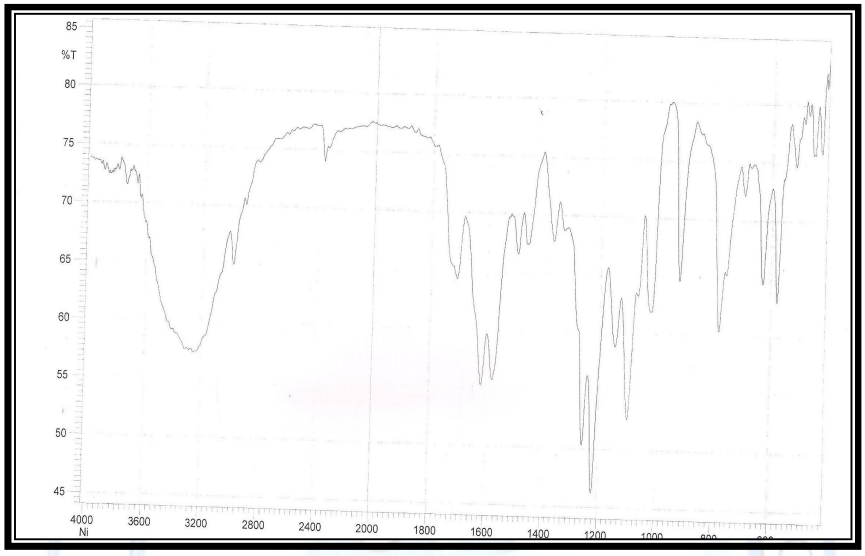


Fig. (2) : FT-IR. Spectrum of [Ni($C_{19}H_{16}N_4O_2$) (H_2O)] Cl_2 Complex

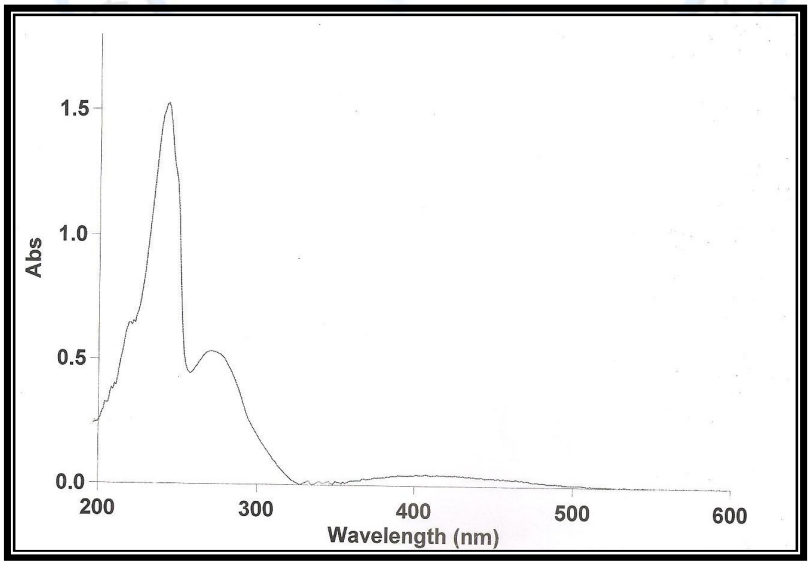


Fig. (3) : UV-Visible Spectrum of ligand (L)

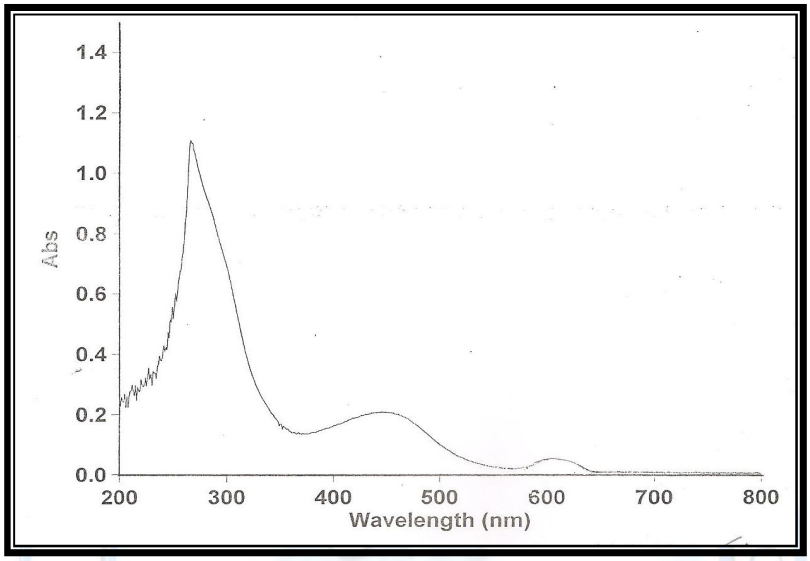


Fig. (4) : UV-Visible Spectrum of Ni (II) Complex

V_M	V_L	$V_{M:L}$	Abs.
1	0.5	1:0.5	0.06
1	1	1:1	0.09
1	2	1:2	0.10
1	3	1:3	0.11
1	4	1:4	0.12

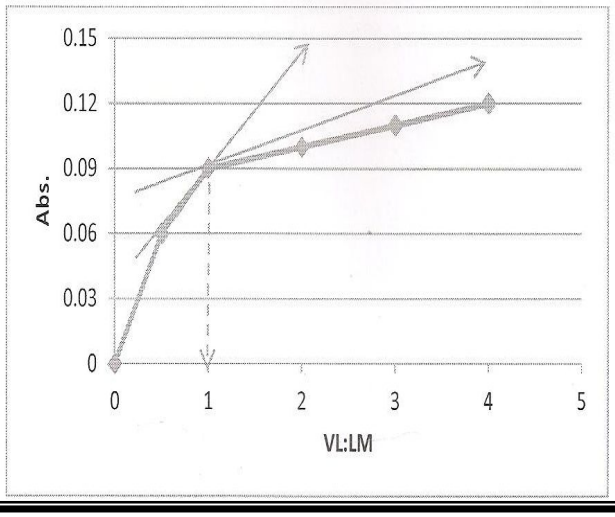
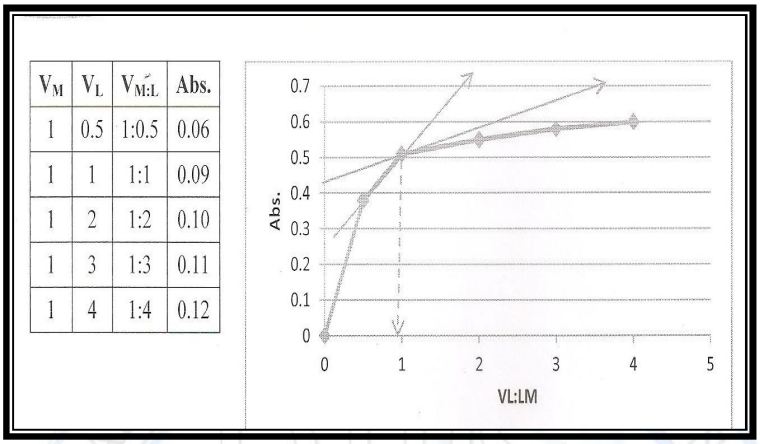


Fig. (5) : Molar- Ratio for Ni: L in λmax 605nm



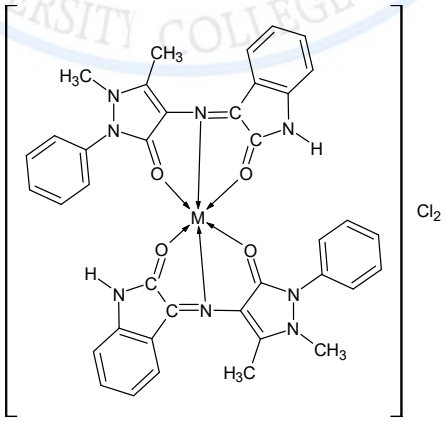
V_M	V_L	$V_{M:L}$	Abs.
1	0.5	1:0.5	0.06
1	1	1:1	0.09
1	2	1:2	0.10
1	3	1:3	0.11
1	4	1:4	0.12

Fig. (6) : Molar- Ratio for Cd: L in λmax 417nm

Suggested Stereo Chamistry Structure for Schiff Base (L) and Its Metal Complexes [E_1-E_6] :

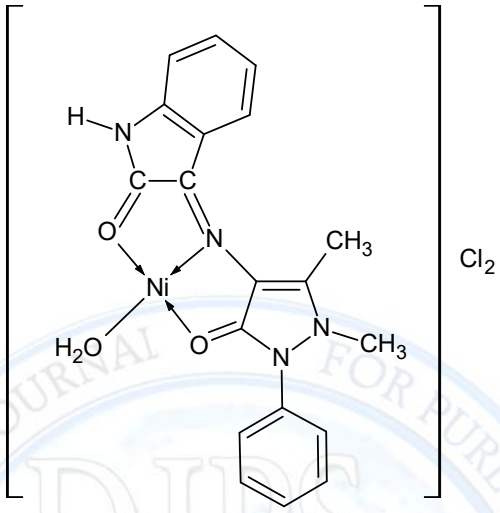
According to the results obtained from elemental and spectral analysis as well as magnetic moment and conductivity measurements, the suggested structure of the above mentioned compounds can be illustrated as follows :

[E_1, E_2, E_4]

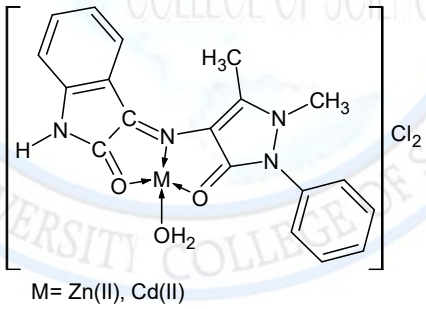


M= Mn(II), Co(II), Cu(II)

[E_3]



[E_5, E_6]



M= Zn(II), Cd(II)

REFERENCES

1. M. H. Tarfder, N. Saravanan, K. A. Crouse and A. M. Ali, "Coordination Chemistry and Biological Activity of Ni(II) and Cu(II) Ion Complexes with Nitrogen-Sulphur Donor Ligands Derived from S-Benzyldit", Transition Metal Chemistry, 26, pp. 613-618, 2001.
2. H. Singh and A. K. Varshney, "Synthetic Structural and Biochemical Studies of Organotion (IV) with Schiff Bases Having Nitrogen and Sulfur Donor Ligands", Bioinorganic Chemistry and Applications, Article ID 23245, pp. 1-7, 2006.
3. T. Jeeworth, H. L. K. Wal, M. G. Bhowon, D. Ghoorhoo and K. Babooram, "Synthesis and Antibacterial Catalytic Properties of Schiff Bases and Schiff Bases Metal Complexes Derived from 2,3-Diaminopyridine", React. Inorg. Met-Org. Chem., 30, 1023, 2000.
4. N. Dharmaraj, P. Viswanalhamurthi and K. Natarajan, "Ruthenium(II) Complexes Containing Bidentate Schiff Bases and Their Anti fungal Activity", Trans. Met. Chem., 26, 105, 2001.
5. V. Alagarsamy, S. Meena and R. Revathi, "AntiHIV, Antibacterial and Antifungal Activities of Some 2,3-Disubstituted Quinazolin-4(3*H*)-Ones", Indian J. Pharm. Sci., 4, 459-62, 2004.
6. V. Alagarsamy and K. V. Ramseshu, "Synthesis and Pharmacological Investigation of Some Novel 2,3-Disubstituted Quinazolin-4(3*H*)-Ones as Analgesic and Anti-Inflammatory Agents", Pharmazie, 58, 233-36, 2003.
7. S. K. Sridhar and M. Sreenivasulu, "Synthesis, Analgesic and Anti-Inflammatory Activity of N-Mannach Bases of (4`-Substituted)-2-Phenylindoles", Indian Drugs, 38, 531-34, 2001.
8. N. Raman, S. Thalamuthu, J. Dhaveedhuraja and M. A. Neelakanan, "DNA Cleavage and Antimicrobial Activity Studies on Transition Metal (II) Complexes of 4-Amino Antipyrine Derivative", J. Chilian Chem. Soc., 53N, 2008.

9. D. A.Skoog, "Fundamental of Analytical Chemistry", 5th Ed., New York, 87, 24411, (1988).
10. R. M.Silverstein, G. C. Bassler and T.Morrill, "Spectrometric Identification of Organic Compounds", 4th Ed., John-Wiley and Sons Inc., New York, London, 1981.
11. M. S. Suresh and V. Prakash, "Preparation and Characterization of Cr(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) Chelates of Schiff Base Derived from Vanillin and 4-Amino Antipyrine", Int. J. Phys. Sci., 5(14), 2203-2211, 2010.
12. A. Patel, S. Bari, G. Talele, J. Patel and M. Sarangapani, "Synthesis and Antimicrobial Activity of Some New Isatin Derivatives", I. J. Pharma. R., 4, 249-254, 2006.
13. K. Nakamoto, "Infrared of Inorganic and Coordination Compounds", 6th Ed., John-Wiely Inc., New York, London, 1997.
14. D. Sutton, "Electronic Spectra Transition Metal Complexes", 1st Ed., Mc.Graw-Hill Publishing, London, 1968.
15. A. D. Kulkarni, S. A. Patil and P. S. Badami, "Synthesis, Characterization and In-Vitro Antimicrobial Studies of Co(II), Ni(II), Cu(II), Mn(II) and Fe(II) Complexes", Int. J. Electrochem. Sci., 4, 717-729, 2009.
16. S. Chandra, D. Jain, A. K. Sharma, "Coordination Modes of a Schiff Base Pentadentate Derivative of 4-Aminoantipyrine with Cobalt(II), Nickel(II) and Copper(II) Metal Ions: Synthesis, Spectroscopic and Antimicrobial Studies", Molecules, 14, 174-190, 2009.
17. J. N. Liu, B. Wu, B. Zhang, Y. Liu, "Synthesis and Characterization of Metal Complexes of Cu(II), Ni(II), Zn(II), Co(II), Mn(II) and Cd(II) with TetradentateSchiff Bases", Turk. J. Chem., 30, 41-48, 2006.
18. A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier Publishing Company New York, London, 1968.
19. K. Siddappa, M. Mallikarjum and C. V. Reddy, "Synthesis, Characterization and Antimicrobial Studies of 3-[(2-Hydroxy-Quinolin-3-Ylmethylene)-Amino]-2-Phenyl-3*H*-Quinazolin-4-One and its Metal(II) Complexes", E. J. Chem. 5(1), :155-162, 2008.
20. A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam, The Netherlands, 2nd Ed., 1984.

Synthesis and Characterization of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) Complexes with new Tridentate (ONO Donor) Schiff Base Ligand

Enaam Majeed Rasheed

تحضير وتشخيص معقدات بعض العناصر الإنتقالية مع ليكاند قاعدة شف ثلاثية السن

أنعام مجيد رشيد

الجامعة المستنصرية، كلية العلوم، قسم الكيمياء

الخلاصة

يتضمن هذا البحث تحضير قاعدة شف كليكاند (L) مشتق من تفاعل 4-أمينو-2،3ثنائي مثيل-1-فنيل-3-بايروزولين-5-أون مع الإيساتين. وقد شخصت تشخيصا دقيقا بالطرق الطيفية المعروفة وهي أطياف الأشعة تحت الحمراء (FT-IR) وأطياف الأشعة فوق البنفسجية-المرئية (UV-Vis) والتحليل الدقيق للعناصر (C.H.N). بعد ذلك تم إستعمال (L) كليكاند في تحضير معقدات الأيونات الفلزية: المنغنيز (II) والكوبلت (II) والنيكل (II) والنحاس (II) والخارصين (II) والكادميوم (II). عزلت المعقدات المحضرة وتم تشخيصها وإقتراح الشكل الهندسي لها عن طريق دراستها بإستعمال تقنية التحليل الدقيق للعناصر (C.H.N) وتقنية الإمتصاص الذري اللهبي للعناصر لتحديد نسبة الفلز (M%) وأطياف الأشعة تحت الحمراء وأطياف الأشعة فوق البنفسجية-المرئية إضافة لقياسات الحساسية المغناطيسية والتوصيلية الكهربائية وتم كذلك دراسة طبيعة المعقدات المتكونة في محلول الإيثانول بإتباع طريقة النسب المولية وقد أعطت هذه الدراسة نتائج متطابقة مع التي تم الحصول عليها في الحالة الصلبة.

الكلمات المفتاحية: تحضير وتشخيص ومشتق البايروزولين وإيساتين وقاعدة شف ومعقدات العناصر الإنتقالية.

Table 1: Analytical and Physical Data of Schiff Base Ligand (L) and Complexes (E_1-E_6)

Comp. No.	Color	M.p.°C	M. Wt g/mol	%Elemental Analysis Found (Calc.)			Metal M% Found (Calc.)	M:L EtOH	Suggested Formula
				C	H	N			
(L)	Orange	140	332	68.32 (68.67)	4.95 (4.81)	16.99 (16.86)	-	-	$C_{19}H_{16}N_4O_2$
E_1	Deep Orange	208	789.9	57.63 (57.72)	4.18 (4.05)	13.91 (14.17)	6.52 (6.95)	1:2	$[Mn(C_{19}H_{16}N_4O_2)_2]Cl_2$
E_2	Dark Brown	184	793.9	57.14 (57.43)	4.08 (4.03)	14.34 (14.10)	7.61 (7.41)	1:2	$[Co(C_{19}H_{16}N_4O_2)_2]Cl_2$
E_3	Brownish-Red	250	479.7	47.29 (47.52)	3.42 (3.75)	11.23 (11.67)	12.63 (12.23)	1:1	$[Ni(C_{19}H_{16}N_4O_2)H_2O]Cl_2$
E_4	Brown	190	798.5	57.58 (57.10)	4.39 (4.00)	14.61 (14.02)	7.72 (7.95)	1:2	$[Cu(C_{19}H_{16}N_4O_2)_2]Cl_2$
E_5	Light Orange	226	486.4	46.38 (46.87)	3.99 (3.70)	11.22 (11.51)	13.12 (13.44)	1:1	$[Zn(C_{19}H_{16}N_4O_2)H_2O]Cl_2$
E_6	Pale Orange	255	533.4	42.35 (42.74)	3.68 (3.37)	10.00 (10.49)	21.36 (21.07)	1:1	$[Cd(C_{19}H_{16}N_4O_2)H_2O]Cl_2$